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The stressed state of a titanile shell operating in a medium with hydrogen

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Abstract. Improving reliability in the operation of equipment operating in a water-containing environment is associated with solving the problem of hydrogen embrittlement of metals. In the absence of a rigorous physical theory, it becomes necessary to predict the carrying capacity of various structures based on the available experimental data showing a decrease in the mechanical properties of materials in contact with hydrogen. In this paper, a solution is given to a physically nonlinear problem of determining stresses in a titanium shell. When integrating resolving equations, the method of SK Godunov's discrete orthogonalization is applied. Due to the fact that hydrogen most noticeably reduces the plastic properties of metals, the construction has revealed a dangerous point with a maximum intensity value of tangential stresses. The regularities of changes in the intensity of shear deformations at the dangerous point of the shell during an emergency pressure increase in the apparatus have been found. It is shown that an emergency pressure increase in the shell may lead to the appearance of plastic deformation zones, and the effect of hydrogen is manifested in the reduction of the breaking load.

1. Introduction

Shell metal elements of structures are widely used as structural elements in various branches of engineering. Sometimes such structural elements during operation work not only under the action of external mechanical loads, but are also under the influence of aggressive media. In this case, it is necessary to take into account the negative impact of aggressive environment on the mechanical properties of the material. Degradation of mechanical properties is one of the important factors that determines the strength and residual resource of technical objects.

Of particular interest recently is the study of the influence of an aggressive hydrogen-containing medium on metals, since hydrogen is one of the most promising sources of raw materials when creating new types of fuel.

It is known that the danger of hydrogen exposure to metal is that this process takes place inside the metal and does not manifest itself by any external signs. Therefore, to assess the strength and life of various structures operating in hydrogen-containing environments, it is necessary to build mathematical models of the mechanics of a solid deformed body, which will use the available experimental data on the effect of hydrogen on the metal.

In the study of the interaction of hydrogen with various metals accumulated a huge theoretical and experimental material. We single out only modern works in [1, 2] which provide an overview of monographs and articles on this subject, and in particular the issues of changing the stress state of structures during hydrogen accumulation.

Titanium alloys are among the construction materials often used in aerospace, chemical and hydrogen energy. Some titanium structural elements in the process of processing and operation in contact with hydrogen-containing media. It is known that hydrogen when interacting with titanium alloys can change their mechanical properties both positively and negatively [3]. The negative effect of hydrogen manifests itself in the form of hydrogen embrittlement, which is characterized by the deterioration of the mechanical properties of titanium alloys at hydrogen concentrations. This is due to the formation of fragile hydrides on the main slip planes and twins.

The tendency of titanium alloys to hydrogen embrittlement depends on the temperature and diffusion rate of hydrogen in the same way as steel. Lowering the temperature decreases the rate of diffusion of hydrogen. With deformation in the metal, hydrogen diffusion processes are accelerated. It is known that during the deformation under the influence of the applied stress, microcracks can arise. The spread of such cracks can then cause brittle fracture.

The effect of hydrogen on titanium alloys was recorded in numerous experiments on stretching of samples, which manifested a change in the shape of the deformation diagram. From the point of view of mechanics, the observed embrittlement of titanium alloys with hydrogen saturation is a decrease in the plastic properties of the material and the destruction of samples with significantly lower residual strains. Consequently, changes in the mechanical properties of the material will also manifest themselves in loaded structural elements subjected to hydrogenation.

Thus, during operation over time *t*, the relationship between stress σ, deformation ε and hydrogen concentration *c* in a structural element can be represented as $\sigma = f(\varepsilon, c, t)$. Therefore, to determine the stress state of structural elements in a hydrogen-containing medium, it is necessary to apply both methods of computational and experimental mechanics.

2. Formulation of the problem

The paper solves the problem of determining the stress state of a thin-walled structure that is operated in a hydrogen-containing environment. It is assumed that the structure is a titanium shell of revolution with thickness h, with variable geometrical and mechanical parameters along the generator. The shell is assigned to a continuous median surface with curvilinear orthogonal coordinates s, θ, γ, where s is the meridional and θ circumferential coordinates, and γ is the direction of the outward normal to the shell surface (Fig. 1). Consequently, $-h/2 \le \gamma \le h/2$.

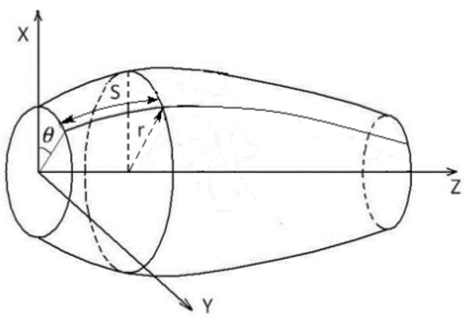

Fig. 1. Shell of rotation in Cartesian coordinate system

The inner surface of the shell is in contact with an aggressive hydrogen-containing medium, from which hydrogen diffuses into the shell under the action of an excessive pressure *p*. It is necessary to determine the stress state of the shell, taking into account the mechanical properties of the material of the structure changing under the influence of hydrogen.

The stress state of a thin-walled structure will be determined using the classical theory of shells in a geometric linear and physically nonlinear formulation. In general, the solution of this related non-

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stationary problem can be represented as a sequence: solving the problem of hydrogen diffusion with determining the distribution of hydrogen concentration, conducting experimental studies on the degradation of the deformation diagram during hydrogen accumulation and determining the stress state of the shell taking into account the physical and mechanical properties of the material.

3. Resolving equations

Since the shell is in contact with hydrogen, it begins to diffuse into the metal wall. The process of diffusional movement of a substance is described by Fick diffusion equations. The change in the concentration of the diffusing substance at each point of the medium is described by the equation [4,5]

$$\frac{\partial c}{\partial t} = D\Delta(c) + f(x, y, z, t) \tag{1}$$

$\Delta = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ – the Laplace operator, $f(x, y, z, t)$ – the function describing the birth or death of diffusing molecules at each point of the medium, D – the diffusion coefficient, c – the concentration of hydrogen in the wall of the shell.

If there are no sources of diffusion, then in expression (1) it is assumed $f(x, y, z, t) = 0$. Since the diffusion equations are completely identical to the heat equation [4], the methods for solving the problems of diffusion and heat conduction are the same. Therefore, the differential equation of diffusion, by analogy with the differential equation of heat conduction, taking into account the absence of heat sources for a thin shell, will have the form [6, 7]

$$\frac{1}{H_1 H_2}\left[\frac{\partial}{\partial s}\left(\frac{H_2}{H_1}\frac{\partial c}{\partial s}\right) + \frac{\partial}{\partial \theta}\left(\frac{H_1}{H_2}\frac{\partial c}{\partial \theta}\right) + \frac{\partial}{\partial \gamma}\left(H_1 H_2 \frac{\partial -}{\partial \gamma}\right)\right] = \frac{1}{D}\frac{\partial c}{\partial t} \tag{2}$$

For the problem of diffusion on the shell surface, similarly to the problem of heat conduction, it is necessary to set some boundary conditions, based on physical considerations. The boundary conditions for the problem under consideration will be the concentrations of hydrogen, which should be known on the surface of the shell. If we accept the assumption of rapid mixing of the hydrogen-containing medium, then we can set the boundary conditions of the first kind

$$c\left(\gamma = -\frac{h}{2}, t\right) = c_H \tag{3}$$

where c_H is the initial concentration of hydrogen on the shell surface.

The volume concentration of hydrogen in metals is measured by its content in ppm (1 cm^3/100 g). It is known that titanium alloys interact very actively with hydrogen and the solubility of hydrogen can reach 40000 ppm, which is two to three orders of magnitude greater than that of steel [8].

The stress axisymmetric state of thin-walled structures using Kirchhoff – Love hypotheses is described by a system of ordinary differential equations of the sixth order [6,9]

$$\frac{d\bar{Y}}{ds} = A(s)\bar{Y} + \bar{f}(s), \qquad (s_0 \le s \le s_L), \tag{4}$$

with boundary conditions

$$B_1\bar{Y}(s_0) = \bar{b}_1, \; B_2\bar{Y}(s_L) = \bar{b}_2 . \tag{5}$$

Here $\bar{Y}$ is the vector function of the desired solution; $A(s), B_1$, B_2 are given matrices of order $k\times n$, $k\times n$ ($k=n/2$); $\bar{f}(s)$, $\bar{b}_1$, $\bar{b}_2$ - are given vectors.

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$$\bar{Y} = \left\{ N_r, N_z, M_s, u_r, u_z, \vartheta_{s,} \right\}, \tag{6}$$

where N_r, N_z is the radial and axial forces; u_r, u_z - similar movements, M_s - meridional bending moment; ϑ_s - the angle of rotation of the normal. The elements of the matrix $A(s)$ and the column vector of free members $\bar{f}$ are given in [6, 7, 12].

4. Numerical methods for solving the problem

In solving the diffusion problem, we use the developed method and computational program for solving boundary value problems of heat conduction. To solve the heat conduction problem, we use the approach based on the fact that the heat conduction equation is replaced by an equivalent variational equation [7], which is solved by the finite element method. The method of solution and the results of the numerical solution of the heat conduction problem for the steel shell structure are given in [10, 11].

The diffusion coefficient necessary to solve the problem characterizes the efficiency of the diffusion movement of hydrogen and has the dimension m^2/s. The value of the diffusion coefficient for the couple of interest diffusing substance - the medium is most often measured experimentally. However, the diffusion coefficient can also be estimated in order of magnitude from simple model considerations [4]. It is known that the speed of the diffusion process is several orders of magnitude less than the speed of heat propagation. Therefore, it can be assumed that there is a stationary temperature field in the shell at any moment of time, and for solving the problem of hydrogen diffusion one can use a numerical method for solving the problem of heat conduction.

For this problem, we take the boundary conditions of the first kind (3). This type of boundary conditions in diffusion problems is called the Dirichlet condition [4]. Consequently, after solving equation (2), the distribution of hydrogen concentration over the shell thickness $c(\gamma,t)$ can be found at any time. The results of the numerical solution of the diffusion problem for various types of boundary conditions for a steel shell are also given in [10, 11].

To integrate the system of equations (4), the method of discrete orthogonalization is used. Godunov [9, 13]. This method allows one to "smooth out" edge effects and is widely used to solve various problems of the theory of shells [6, 9, 12].

When solving this problem, taking into account possible plastic deformation, the physically nonlinear problem will be described by a system of differential equations (4), and the relationship between stress and deformation will be linearized by the method of additional deformations. This relationship is presented in the form of Hooke's law, but with additional members that take into account the dependence of the mechanical properties of the material on the deformation and temperature [6, 7]. We assume that this relationship will take into account the change in the mechanical properties of materials and the concentration of hydrogen. In this case, the volume stress state of the shell will be compared with the uniaxial state with simple stretching of the sample at c= *const* [6, 7].

$$S_\partial^* = \frac{\sigma}{\sqrt{3}}, \ \Gamma^* = \frac{1+\nu}{\sqrt{3}}\varepsilon, \tag{7}$$

where σ and ε are stresses and strains during simple stretching of the sample, and ν is Poisson's ratio. The intensities of tangential stresses and shear deformations in the shell S_∂ and Γ are defined as

$$S_\partial = \sqrt{(1/3)\cdot(\sigma_s^2 - \sigma_s\sigma_\vartheta + \sigma_\vartheta^2)}, \tag{8}$$

$$\Gamma = \sqrt{(1/6)\cdot[(\varepsilon_s - \varepsilon_\gamma)^2 + (\varepsilon_\gamma - \varepsilon_\vartheta)^2 + (\varepsilon_\vartheta - \varepsilon_s)^2]}, \tag{9}$$

where σ_s and σ_ϑ are respectively the meridional and circumferential stresses, and $\varepsilon_s, \varepsilon_\vartheta, \varepsilon_\gamma$ are the components of the deformations along the meridian, the circumference and the normal to the shell surface.

5. Experimental studies necessary to solve the problem

As noted above, to solve this problem, experimental dependencies between stress and strain, varying in the process of hydrogenation, are necessary. Of all the variety of published experimental data for samples in contact with hydrogen-containing media, it is not so easy to select data that fully satisfies the necessary conditions of the problem to be solved. In order to “close” the task, we use the experimental data for samples of titanium alloy VT20 in the initial state and after hydrogenation to saturation.

For samples of the first rolled strip thickness of 10 mm were cut out along and across the plate rolling direction, as manufacturing technology induces anisotropy in mechanical properties. From these plates are ground on four samples in diameter and 2 mm length. For the hydrogenation of the titanium plate as the hydrogen source used titanium hydride, which is at a temperature of 400 degrees starts to release hydrogen. With a further increase in temperature, an increase in pressure was observed, since the plate did not have time to absorb all the hydrogen. Heating was carried out at a temperature of 850 degrees. To further saturate with hydrogen, the thermal mode of hydrogenation included a slow stepwise (20 minutes each) decrease in temperature to 600 degrees and cooling with a furnace. In tensile tests on these specimens, a high-rigidity loading device with parallel rods was used [14].

Figure 2 shows the conditional deformation diagrams. Curves 1 and 2 correspond to the samples machined from the unharmonized plate across and along the rolling direction, respectively. Curves 3 and 4 reflect the results of tensile testing of specimens machined from a hydrogen-containing plate.

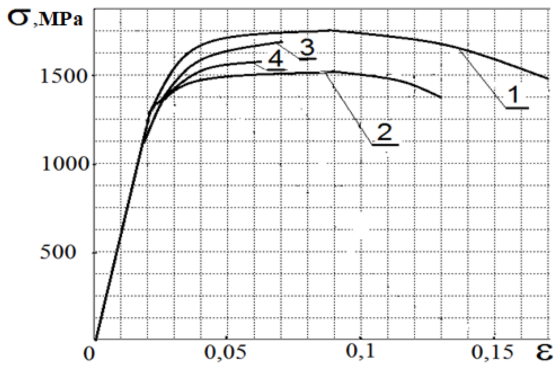

Fig. 2. Conditional diagrams of deformation of the alloy VT20

From the stretching curves shown in Fig. 2, it can be seen that the strength of the hydrogenated titanium specimens varies slightly, and the deformation during fracture significantly decreases both along and across the rolling. A decrease in the ultimate strength when exposed to hydrogen is characteristic of many titanium alloys [15]. A significant reduction in the deformation of the sample will determine the ultimate load of structural failure. Therefore, the phenological effect of material embrittlement must be taken into account in models of the mechanics of a deformed body for structures made of titanium alloys when evaluating their strength.

Since the existing various methods for determining the hydrogen content in titanium alloys require special expensive equipment [16], it was not possible to determine the residual hydrogen concentration in samples for this experiment. Therefore, to determine the stress state, there are only dependencies $\sigma = f(\varepsilon)$ at T = 25 C^0 without hydrogen and with residual hydrogen along and across the rolling direction. We will use mechanical data (Fig. 2), expressed by curve 1 (without hydrogen) and curve 3 (with residual hydrogen).

6. Solution example

As an example, it was determined the stress state of the thin-walled case of the apparatus of special equipment. The structural design of the housing is shown in Figure 3. (dimensions are shown in centimeters). This case is made of steel 12X18H10T. The housing in operation is in contact with a hydrogen-containing medium. The calculation was made when replacing steel with titanium alloy VT20. The thin-walled case is approximated by five shell elements: a plate 0≤s≤0.088 m, a torus 0.088≤s5≤0.40216 m and three cylindrical sections of different thickness. The wall thickness of most of the body is h = 0.018 m, the median radius of the cylindrical part is R = 0.4 m. The body is loaded with internal pressure P = 10 MPa. Operating temperature 20C°. In the calculation, the mechanical properties of the hull are expressed by dependencies without hydrogen (curve 1, Figure 2) and with residual hydrogen (curve 3, Figure 2). Boundary conditions (5): on the left side with $s = s_0$ a pivotally mobile support $M_S = u_r = N_Z = 0$, on the right side with $s = s_L$ a pivotally stationary support $M_S = u_r = N_Z = 0$. As a result of the operation of the apparatus, hydrogen diffuses into the body wall, which leads to a change in the mechanical characteristics of the material and a drop in its strength.

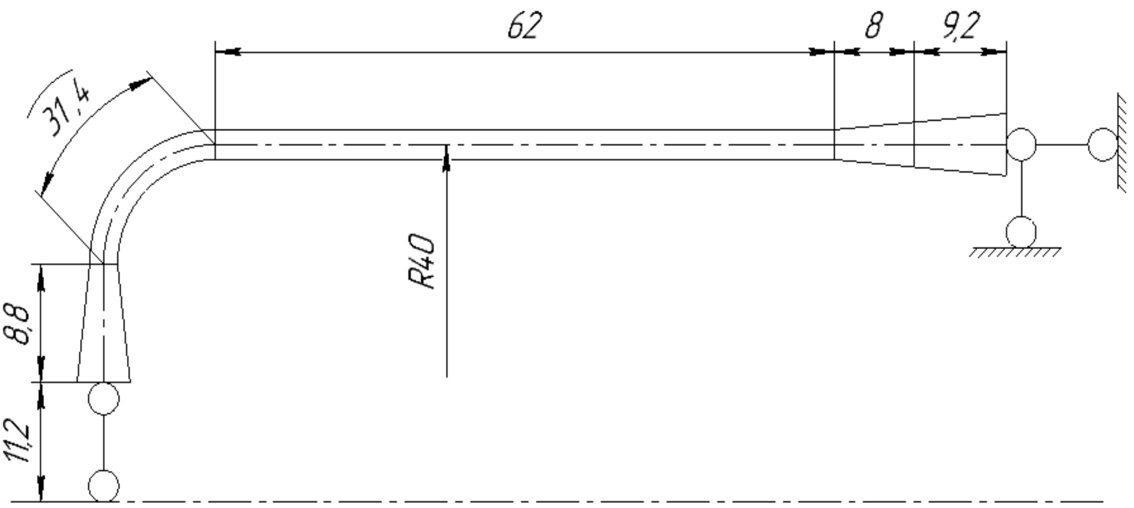

Fig. 3. Enclosure

For this problem, equation (2) was not solved, since the concentration measurement during hydrogenation in the experiment for uniaxial tension was not performed. If it is necessary to solve such a problem, the method of their solution is described in detail in [10,11].

To determine the effect of hydrogenation on the strength of the titanium case, its stress state (6) with mechanical properties without hydrogen and with mechanical properties after saturation with hydrogen was determined.

Figure 4 shows the calculated distribution of the meridional σ_s and circumferential σ_θ stresses along the coordinate *s* on the inner surface of the shell at a pressure of *P* = 10 MPa. The asterisks show the stresses on the outer surface of the shell. From the results of the calculation it follows that the shell material works even in the elastic region of the diagram. Since the elastic modulus is the same for mechanical properties without hydrogen and with hydrogen ($E = 1{,}1 \times 10^5$ MPa), the calculation results are the same.

Even with an increase in pressure to *P* = 20 MPa, the shell material is still working in the elastic region of the deformation diagram due to the high proportionality limit of the alloy $\sigma_{пц}$ = 1100 MPa.

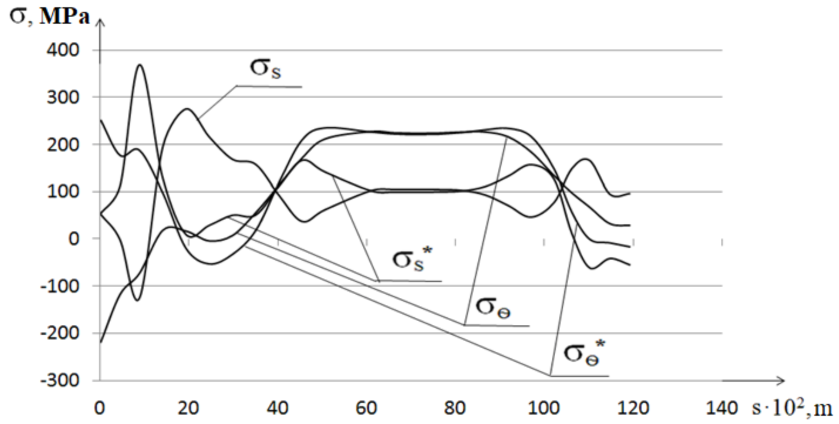

Fig. 4. The change of the meridional σ_s and circumferential σ_θ stresses along the coordinate s on the inner and outer surface of the shell

With a further increase in pressure, caused, for example, by an emergency situation, the task becomes physically nonlinear. So, at a pressure of P = 30 MPa, it took five or six approximations to solve a nonlinear problem in order to achieve the required accuracy of the solution of 1%. At the same time, zones of plastic deformation appear in the shell. It is of interest to estimate the limiting pressure in the apparatus, at which its destruction is possible. As an indicator of the ultimate state of a material at a dangerous point in a structure, the integral power characteristic can be used - the intensity of tangential stresses S_∂ calculated by the formula (8) or the deformation characteristic - the intensity of the shear deformations Γ calculated by the formula (9).

Figure 5 shows the change in the intensity of tangential stresses S_∂, defined by formula (8), with increasing pressure p for the most loaded point of the outer surface shell (s = 0.088 m) - the beginning of the torus-shaped section. Curve 1 corresponds to the calculation for the accepted mechanical properties of a titanium alloy without hydrogen, and curve 2 with residual hydrogen.

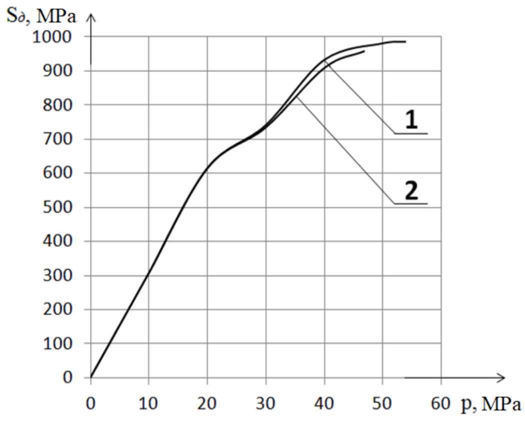

Fig. 5. The change in the intensity of tangential stresses

Figure 5 illustrates the nonlinearity of the problem depending on the external load. With an external pressure of more than P = 20 MPa, regions with residual (plastic) deformations begin to form in the shell. That is, the linear relationship between the external load and the resulting stresses is violated. The difference in the values of the limiting pressure, when the intensity S_∂ reaches the limiting intensity value S_∂^* for the material, calculated by the formula (7), is about 10 MPa.

As noted above, in hydrogenated titanium samples, the deformation during fracture is significantly less than in conventional samples. This embrittlement effect must be taken into account when assessing the strength of structural elements in a complex stress state. This can be done, apparently, if we limit the intensity of the shear deformations Γ for the hydrogenated sample to the limiting deformation when Γ^*_{ext} =0.045, expressed by the relation (7). The ultimate deformation at failure for the sample in the initial state is much higher Γ^*_{ext} =0.12.

Figure 6 shows the change in the intensity of shear deformations Γ on the outermost, most loaded surface of the shell and at the most loaded point of the shell (s=0.088 m). Curve 1 corresponds to the calculation for the adopted mechanical properties expressed by curve 1 in Figure 2 (without hydrogen), and curve 2 to the calculation for the adopted mechanical properties expressed by curve 3 Figure 2 (with residual hydrogen). From the figure (curve 2), it follows that the limiting pressure that the shell can hold of the hydrogenated material is P = 46.9 MPa. Due to the plastic properties of the non-hydrogenated material (curve 1), the limiting pressure is P = 54.6 MPa.

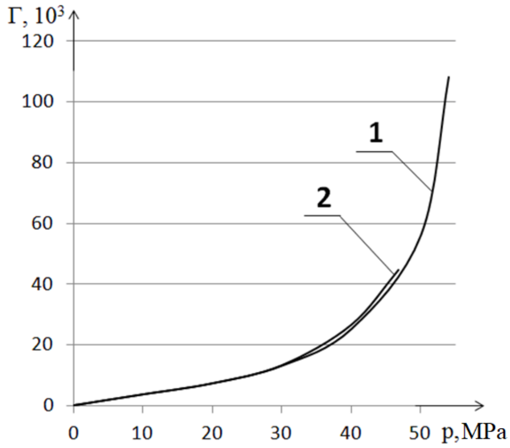

Fig. 6. The change in the intensity of shear strain Γ on the outer surface of the shell

The hydrogenation of the shell not only reduces the limiting pressure, reducing the margin of damage, but also changes the nature of the destruction. Accidental viscous destruction of the apparatus in the initial state after significant plastic deformations can be replaced by quasi-brittle after saturation with hydrogen. The above calculation gives not only a qualitative, but also a quantitative idea of the specified shift. In the presence of intermediate data on changes in material properties during hydrogenation, a complete description of the process of transition from ductile sheath to brittle fracture is possible.

Conclusion

Thus, using the modern numerical and experimental methods, the stress state of a thin-walled titanium shell, which is operated in an environment with hydrogen, is determined. Actual stresses and their invariants are determined by solving a physically nonlinear boundary value problem. It is shown how the known embrittlement effect of titanium alloy observed in the experiment on samples under the influence of hydrogen, manifests itself in the shell structure by reducing the ultimate fracture pressure and changing the nature of fracture.

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